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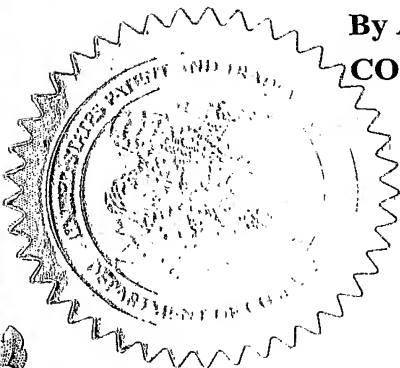
February 28, 2005

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APPLICATION NUMBER: 60/539,101

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By Authority of the  
COMMISSIONER OF PATENTS AND TRADEMARKS



*M. Tarver*

M. TARVER  
Certifying Officer

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60/539101

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**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.

INVENTOR(S)					
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)			
Yifat	BAREKET	Re'ut, ISRAEL			
Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
BROMINATED POLYMERS, AND FIRE RETARDANT ARTICLES COMPRISING THEM					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input checked="" type="checkbox"/> Customer Number:		20529			
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ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification Number of Pages 37		<input type="checkbox"/> CD(s), Number _____			
<input type="checkbox"/> Drawing(s) Number of Sheets _____		<input checked="" type="checkbox"/> Other (specify) Assignment,			
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.					FILING FEE Amount (\$)  \$ 80.00
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees.					
<input checked="" type="checkbox"/> The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 14-0112					
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.					
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

[Page 1 of 2]

Respectfully submitted,

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Date January 27, 2004

REGISTRATION NO. 41,827

(if appropriate)

Docket Number: 25959

**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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13281 U.S. PTO  
MAIL STOP PROVISIONAL PATENT APPLICATION  
Attorney Docket No. 25959

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Yifat BAREKET

Serial No. NOT YET ASSIGNED

Filed: January 27, 2004

For: **BROMINATED POLYMERS, AND FIRE RETARDANT ARTICLES COMPRISING THEM**

TRANSMITTAL LETTER

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

Submitted herewith for filing in the U.S. Patent and Trademark Office is the following **PROVISIONAL APPLICATION**:

- (1) Transmittal Letter
- (2) Cover sheet for filing **Provisional Application**
- (3) 37 page Provisional Application consisting of:
  - 30 pages Textual Specification,
  - 7 pages of Claims,
  - 0 page of the Abstract,
  - 0 sheets of Drawings;
- (4) Assignment and Recordation Cover Sheet;
- (5) Check No. 20264 \$ 80.00 for filing fee as a small entity;
- (6) Check No. 20265 \$ 40.00 for recordation fee;
- (7) Postcard for early notification of serial number.

The Commissioner is hereby authorized to charge any deficiency or credit any excess to Deposit Account No. 14-0112.

Respectfully submitted,  
**NATH & ASSOCIATES PLLC**

By: 

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GMN/LCH/dd:APPL.trans

## **BROMINATED POLYMERS, AND FIRE RETARDANT ARTICLES COMPRISING THEM**

### **FIELD OF THE INVENTION**

This invention relates to brominated polymers, dispersions thereof, and uses of such polymers and dispersions.

### **BACKGROUND OF THE INVENTION**

It is known in the art to include bromine-containing additives in articles such as fabrics, coatings, and adhesives, in order to render them fire-retardant. If such additives are of small molecular weight, and not chemically bond to the matrix, they might diffuse out of the product (especially if the product is frequently washed, like in the case of fabrics), and fire retardancy decreases. Furthermore, the drainage of manufacturers and users of such products may contain brominated additives, which might cause environmental problems.

One object of the present invention is to provide novel brominated substances that may be used as additives for rendering an article fire retardant. Other objects will be made clear to the reader from the following description and claims.

### **RELATED ART**

The following publications may be helpful in understanding the background of the invention. An appearance of a publication under this title, however, should not be construed as applying that the publication is relevant to the patentability of the invention.

1. US patent application publication no. 2002/24042, describing dispersions and terpolymers of PBBMA;

2. US 5,072,028, describing a process for the preparation of PBBMA and related compounds;
3. US 4,728,463, describing brominated styrene-maleate copolymers;
4. US 4,412,051, describing fire resistant copolymers of bromostyrene and another monomer, preferably, acrylonitrile;
5. US 5,290,636 describing flame retardant latex coatings, which comprise copolymers of ring-halogenated aromatic monomer units, alkyl acrylate/methacrylate monomer units, and optionally another monomer unit; and
6. US 5,276,091 describing polymeric compositions wherein a base polymer is blended with a stable interpolymer prepared by copolymerizing a brominated monovinyl aromatic monomer, a methacrylic acid ester and, optionally, an ethlenically unsaturated nitrile.

## SUMMARY OF THE INVENTION

The present invention provides a copolymer made of at least one bromine-containing monomer, and at least one other monomer. Bromine containing monomers included in the copolymer of the invention are of the formula A-B-C wherein A is a phenyl, substituted with 3-5 bromine atoms, B is a C<sub>1</sub>-C<sub>4</sub> alkyl, optionally substituted with 1-8 bromine atoms, and C is an acrylic or methacrylic group. The copolymer of the invention is characterized in having bromine contents of at least 20%. All the concentrations expressed herein by % refer to w/w percentage, unless otherwise is indicated.

The group A defined above may be substituted with 3, 4, or 5 bromine atoms, where 5 is most preferable. Independently, the group B is a lower alkyl, which may have 1, 2, 3, or 4 carbon atoms, each of which may independently have none, 1, or 2 bromine substituents.

Some examples for brominated monomers in accordance with the present invention are tri, tetra, and penta bromo benzyl acrylate, tri, tetra, and penta bromo benzyl methacrylate, tri, tetra, and penta bromo phenyl ethyl (meth)acrylate, tri, tetra, and penta bromo phenyl mono-, di-, tri-, or tetra-bromo ethyl (meth)acrylate, tri, tetra, and penta bromo phenyl mono-, di-, tri-, tetra-, penta-, or hexa-bromo propyl (meth)acrylate, and tri-, tetra-, or penta-bromo phenyl mono-, di-, tri-, tetra-, penta-, hexa-, septa-, or octa-bromo butyl (meth)acrylate. Penta bromo benzyl acrylate will be referred to hereinafter as PBBMA.

The polymer of the invention includes monomers of at least two different structures, and therefore, may also be named copolymer. Thus, the terms *polymer* and *copolymer* are used herein interchangeably.

According to one embodiment the polymer of the invention has bromine contents of 60-70%, according to another embodiment the bromine contents is between 25 and 50%, and according to another embodiment 20-35%. Polymers of different bromine percentage may be useful for different applications and corresponding flame retardancy (FR) standards.

Additionally to the bromine containing monomer, a polymer according to the present invention has at least one non-brominated monomer, which may be a specialty monomer, or a non-specialty monomer.

Non-limiting examples of functions that may be attributed to specialty monomers include cross-linking, surface active, or adhesion promoting. In some cases, a single specialty monomer may have more than one function, for instance, N-methylol acryl amide functions both as a surfactant and as an adhesion promoter, which improves the adhesion of the polymer to textiles. Non-limiting examples of specialty monomers that may be used according to the invention are sodium salt of 2-acrylamido-2-methyl propane sulphonic acid, betal-carboxymethyl acrylate, ammonium allyloxypolyethoxy(10)sulphate, laurethoxy(23)methacrylate, laurethoxy(25)methacrylate, allyl methacrylate, hydroxyl ethyl methacrylate, glycidyl methacrylate, ammonium salt of  $\alpha$ -sulfo- $\omega$ -[1-(Alkoxy)methyl-2-(2-propenyloxy)ethoxy]- $\omega$ -hydro-poly(oxy-1,2,-ethanediyl), ammonium salt of  $\alpha$ -[1-

(Alkoxy)methyl-2-(2-propenyloxy)ethoxy]- $\omega$ -hydro-poly(oxy-1,2,-ethanediyl), Ditrithymolpropane tetraacrylate, Ethoxylated trimethylolpropane triacrylate, and Trimethylolpropane triacrylate. Such specialty monomers are sold under trade names such as AMPS2405 (manufactured by Lubrizol), Beta C, DVP-010, Lem 23, Lem25 (all by Bimax Inc.), HEMA (by Laporte), Akeda Reasope SR-10, Akeda Reasope SR-20, Akeda Reasope SR-30, all by Asahi Denka, and SR355, SR454, SR351 (all by Cray Valley).

Non-limiting examples of non-specialty monomers that may be used according to the present invention are acrylic monomers, vinyl acetate, styrene, and styrene derivatives such as  $\alpha$ -alkyl styrene, and particularly  $\alpha$ -methyl styrene.

Preferable acrylic monomers are acrylamide, acrylic acid, methacrylic acid, acrylonitrile, butyl acrylate, ethyl acrylate, 2-ethyl hexyl acrylate, and methyl methacrylate.

A polymer according to the invention is typically made of between two and six different monomers. When very high bromine content is desirable, the non-brominated monomers are typically specialty monomers.

A specific group of monomers useful according to the present invention are of acrylic structure, namely, monomers of the formula  $R_1CH=CR_2C(O)A$ , wherein

A is selected from the group consisting of  $OR_3$ ,  $NR_3R_4$ , and  $CN$ ; and

$R_1$ ,  $R_2$ , are each independently selected from H or alkyl, said alkyl being linear or branched, and each of  $R_3$  and  $R_4$  independently may be H, alkyl, alkenyl, alkoxy, polyalkoxy, alkanol, or ether, each of which may be linear or branched, substituted or unsubstituted. As may be apparent from the examples given below, the carbon-containing R groups (namely, those groups of  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  that contain carbon) have usually between 1 and 15 carbons, although some of them may at times contain more carbon atoms. The alkyl R groups are typically of 1-4 carbon atoms.

Among the above mentioned acrylic monomers, those with  $R_3$  or  $R_4$  other than alkyl are typically specialty monomers.



According to another aspect of the present invention, there is provided an aqueous polymeric dispersion of a bromine-containing polymer, wherein the solid content in said dispersion is at least 40%, typically 40-65%, most typically 40-55%.

The term dispersion is used herein to refer to solid particles dispersed in liquid medium. In a dispersion, the particles do not agglomerate, at least on a time scale of practical interest, and this is usually achieved by including therein suitable surface active agents. According to the invention, two or more surface active agents are usually required.

Surface active agents, surfactants, emulsifiers, and dispersants, are all terms that are used herein interchangeably.

It should be noted that it is preferable to use such surfactants that are useful in all the stages of the polymerizing procedure, starting with stabilizing a dispersion of the brominated monomer, through stabilizing pre emulsion or pre dispersion and allowing efficient polymerization reaction between the different monomers, and ending with stabilizing the polymeric aqueous dispersion obtained eventually. This complicated task is usually accomplished in accordance with the present invention by two or more surfactants. Surfactants that were found by the inventor to be most suitable according to the present invention are nonionic and/or anionic surfactants. Among the nonionic surfactants, alkyl phenol based surfactants are particularly useful. It should be noted, that some countries tend to limit the use of alkyl phenols, since these compounds are suspected as being non-friendly to the environment and to human health. Therefore, substitutes to alkyl phenols are being developed, and such substitutes are expected to be also very useful in accordance with the present invention.

Of the anionic surfactants, of most particular interest are alkyl aryl based, such as alkyl aryl sulphonic acid or alkyl aryl sulphonate.

Non-limiting examples to liquid mediums in which a brominated copolymer may be dispersed in accordance with the present invention are water, glycols, and mixtures thereof.

Preferably, the bromine-containing polymer, which is dispersed in the dispersion of the invention, has a bromine content of at least 20% (w/w), and is in accordance with the first aspect of the invention, as described above.

Typically, the aqueous polymeric dispersion has a high density (comparing to commercial acrylic polymers), of above 1.2 g/cc, usually between 1.2 and 1.7gr/cc, which makes it difficult to stabilize its aqueous dispersion. The dispersion is stabilized by surfactants, and usually by a combination of two or more surfactants, each of which may be reactive (i.e. become part of the polymer chain) and/or non-reactive (i.e. remain as independent substance in the dispersion).

Preferable aqueous polymeric dispersions according to the invention have a particle size of 2000nm and smaller, preferably between 50 and 1000nm, more preferably between 80 and 400nm. Typically, the molecular weight of polymers according to the invention is 500,000 and above, preferably above 1,000,000.

Polymeric aqueous dispersions according to the invention proved to be stable for at least six months at 5-35°C without direct sunlight. Conventional additives, such as propylene glycol may extend this temperature range to about -7° - +35°C.

According to another aspect thereof, the present invention provides fire-retardant products comprising a bromine-containing polymer together with antimony-oxide (hereinafter AO). The AO is usually added to the aqueous polymeric dispersions in methods known in the art *per se*, namely, as commercially available dispersion, added to the final dispersion after its stabilization. Nevertheless, the invention also encompasses products and dispersions that include AO, which was added in other manners. One non-limiting example for such products is a dispersion wherein the AO is added during polymerization stage, as demonstrated in Example 12 below. Preferably, the bromine-containing polymer, dispersed in the dispersion that renders the products of the invention fire retardant, has a bromine contents of at least 20% (w/w) and is by itself in accordance with the first aspect of the present invention.

In the context of the present application and claims a product is considered fire retardant if it meets international standards, such as standard CFR16/1615 for fabrics, standard -ASTM D3806 for paints, and standard ASTM D2859, BS 476-7, DIN 4102-1, ISO1182 for building materials.

Non-limiting examples to products according to the invention are textiles, non-woven fabrics, paints, coatings, and adhesives.

In case of textiles according to the invention, polymers of the invention may be applied thereto mainly by means of topical application of a dispersion according to the invention or impregnation of such dispersion into the treated textile. Methods for topical application include, for instance, spraying, padding, or printing. Since these methods (including impregnation are commonly used in the textile industry, the present invention does not require any unique production line dedicated to the treatment of the textiles to make them fire retardant.

Another advantage that may be associated with the use of textiles according to the invention is that the drainage of the manufacturing facility as well as that of the users does not contain free bromine compounds.

Many textiles are designed to be hydrophobic, in order to retain their color strength, to allow them to remain stain free, and to eliminate water penetration through the textile. The present invention is suitable for such applications, especially if a polymer with a non-brominated hydrophobic monomer is used. Non-limiting examples of monomers to be used for obtaining a hydrophobic fire retardant textile according to the invention are butyl Acrylate, 2-ethyl hexyl acrylate, and styrene.

Typically, polymers in accordance with the invention have Tg of between -20°C and 70°C. It is interesting to note that according to the invention it is also possible to obtain polymers with Tg lower than 0°C. This may be achieved by using polymers with non-brominated monomers having a low Tg, of typically lower than 0°C, which results in a soft hand fire retardant textile that is out of reach of most state of the art methods. Non-limiting examples of monomers with Tg lower than 0°C are butyl Acrylate, ethyl Acrylate, and 2-ethyl hexyl acrylate.

Another advantage that may be associated with textiles that are made fire retardant in accordance with the present invention is that they remain transparent without affecting the final color of the textile. However, such transparency is typically obtained only in such textiles that were treated with dispersions according to the invention that had a particle size of between about 100 and about 350nm.

Similar advantages may be obtained also by applying the dispersion or polymer of the invention to non-woven fabrics. Furthermore, in case of non-woven materials, these may be made by the chemical bond method, in which case, a polymer in accordance with the present invention may be used for chemically bonding fibers of the non-woven fabric and at the same time rendering said fabric fire-retardant.

Naturally, non-woven fabrics may also be made fire retardant by topically applying to them a dispersion according to the invention, for example, by printing, spraying, , and the like, or by impregnation.

Non-woven articles may frequently benefit from having a soft, non-fragile structure. This may be obtained with polymers of the invention, wherein the non-brominated monomer is of a low Tg, preferably, lower than 0°C. Non-limiting examples to such monomers are butyl acrylate, ethyl acrylate, and 2-ethyl hexyl acrylate.

Regarding to paints, coatings and adhesives, since these are typically water-based acrylics, the dispersion of the present invention may easily be made compatible with such products, do not shorten their shelf life, neither adversely affects their effectiveness.

According to another of its aspects, the present invention provides a method for obtaining an aqueous dispersion of a co-polymer containing at least a first monomer and a second monomer, wherein said second monomer is at least partially dissolved in said first monomer, and reacts to polymerize therewith in the presence of water surfactants; the method being characterized in that the first monomer is a brominated aromatic compound.

Preferences for the first monomer in accordance with this aspect of the invention are the same as for the brominated monomer in accordance with the other aspects of the invention.

The second monomer is preferably styrene or a derivative thereof, such as  $\alpha$ -alkyl styrene.

According to one embodiment, the method comprising:

- (i) dissolving said first monomer in a first liquid to obtain a solution, wherein said first liquid includes said second monomer optionally together with surfactants;
- (ii) mixing said solution with water and optionally also with surfactants to obtain a stable emulsion comprising water, surfactants, and said first monomer; and
- (iii) reacting said stable emulsion with an initiator to obtain an aqueous dispersion of a polymer containing at least said first monomer and said second monomer.

According to one embodiment, the first liquid does not include surfactants, and these are added only in (ii). Preferably, this method of the invention is utilized to obtain an aqueous polymeric dispersion in accordance with the invention (i.e. at least 40% solid content, etc.), and the polymer dispersed therein is also in accordance with the invention (at least 20% bromine content, etc.)

One embodiment of particular interest is where at least one of the surfactants is reactive, and the obtained polymer contains it in the polymeric chain.

Another embodiment of particular interest is a method as described herein, wherein the first and second monomers react with at least one other monomer, such that the polymer obtained by the method is a copolymer of the first monomer, the second monomer, and this at least one other monomer. All non-brominated monomers mentioned in relation to the other aspects of the invention may be useful in this embodiment.

It should be noted that the solution of the first monomer dissolved in the second monomer is not necessarily clear, and may include non-dissolved particles

of the first monomer. However, usually, the solution is prepared to appear clear to the naked eye.

According to another aspect of the present invention there is provided a method for obtaining an aqueous polymeric dispersion having a polymeric particles of a first size, by reacting a dispersion of monomers having particles of a second size, wherein said second size is larger than said first size, comprising: reacting said dispersion with a mixture comprising said other monomers, and stirring the reaction mixture at about 200-300rpm and adding reactive substances to the mixture at a rate of between 1 and 10ml per minute, while keeping the temperature at about 70-90°C.

#### **DETAILED DESCRIPTION OF THE INVENTION**

In order to understand the invention and to see how it may be carried out in practice, several exemplary embodiments will now be described, by way of non-limiting example only. In all these examples, the order of adding the various ingredients may be of crucial importance.

In particular, presented here is a list of substances that were used by the inventor for carrying out the invention in accordance with the following examples. The invention is not limited to the substances listed herein, however, they should suffice for carrying out the following examples.

In this regard, it should be noted that some of the surfactants listed below are commercially available when they are water-diluted. In other cases, the user should dilute them in water before use. When the inventor diluted a surfactant from the list below in order to use it in accordance with the invention, the used dilution is mentioned in the list. Amounts mentioned in the Examples below are always of diluted surfactants.

#### **LIST OF USEFUL SUBSTANCES**

##### **General**

**PBBMA** – pentabromo benzyl acrylate. (FR-1025M. Dead Sea Bromine Group).

**APS** –Ammonium Per Sulphate –(Degussa, Caldig, Stan Chem)

**Formosul** – Sodium Formaldehyde Solphoxylate dihydrate (Stan, Transpek-silox)

**TBHP** – tert-Butylhydroperoxide 70% (Peroxide Chemie, Witco)

**Nyacole 1550** –Antimony pent oxide dispersion. (Nyacol Nono )

**Nyacole 1540N** - Antimony pent oxide dispersion. (Nyacol Nono)

**Nyacole 1550PH7**- Antimony pent oxide dispersion. (Nyacol Nono )

**Surface Active agents:****Aerosol OT75** – Sodium Dioctyl sulphosuccinate in ethanol/water (Cytec)

**NP6** – Nonyl Phenol + 6 Ethylene oxide (Sasol)

**NP9** – Nonyl Phenol + 9 Ethylene oxide (Sasol)

**Synperonic NP10** - Nonyl Phenol + 10 units of Ethylene oxide(Uniqema)

**Synperonic NP12** - Nonyl Phenol + 12 units of Ethylene oxide(Uniqema)

**Synperonic NP10** - Nonyl Phenol + 10 units of Ethylene oxide(Uniqema)

**Synperonic NP17** - Nonyl Phenol + 17 units ofEthylene oxide(Uniqema)

**NP20** – Nonyl Phenol + 20 units of Ethylene oxide (Sasol)

**NP30** – Nonyl Phenol + 30 units of Ethylene oxide (Sasol)

**Synperonic NP40** - Nonyl Phenol + 40 units of Ethylene oxide(Uniqema)

**Otix40** – Octyl phenol ethoxylate (Condea)

**Emulgaten CO 55**- Alkyl polyglycol ether (Condea )

**Emulgante AS25** – Alkyl polyglycol ether (Condea )

**Byk190** – Sol. Of a polyfunctional polymer with anionic/ nonionic character (Byk chemia)

**Byk 380** – Dipropylene glycolmethyl ether (Byk chemia)

**Byk 154**- Ammonium acrylate copolymer (Byk chemia)

**Zoropol SLS**- Sodium lauryl sulfate (Zohar detergent Factory)

**Zoropol AN** – Ammonium nonoxynol 9 sulphate (Zohar detergent Factory)

**Labs60** – Sodium Alkylbenzene sulfonate (Zohar detergent Factory)

**Labs100** – Dodecylbenzene sulphonic acid (Zohar detergent Factory)

**Solsperse 44000** –(Avecia)

**Ethylan Co-55** – Cethyl-Oleyl Alcohol Ethoxylate (Akcros)

**Imbentin U60** – Branch oxo alcohol C11+6 ethylene oxide (Dr. Kolb)

**Lutensol AT80** – Fatty alcohol ethoxylated. (BASF)

**Antifoam:**

**Antifoam**– Blend of hydrocarbon & nonionic (Stockhausen)

**Foamaster 3082** – fatty acid ester and salts in hydrocarbons alkylate (Nymco)

**Darpo 2162** – (Elementis)

**Moussex 3029 HL** - (Synthron)

**Foamaster 50** – (Cognis)

**Special Monomers:**

**N-Methylol Acryl amide** – N-(Hydroxymethyl)Acrylamide (our synthesis product)

**Glycidyl Methacrylate** – (Dow)

**AMPS2405** —2-acrylamido -2 -methyl propane sulphonic acid, sodium salt (Lubrizol)

**Beta C** – Beta-carboxyethyl acrylate (Bimax)

**DVP – 010** –Ammonium allyloxypolyethoxy(10) Sulfate (Bimax inc.)

**Lem 23** – Laurylethoxy (23) methacrylate (Bimax)

**Lem 25** – Laurylethoxy (25) methacrylate (Bimax)

**Allyl Methacrylate** – (Shinwa trading)

**HEMA** – Hydroxy ethyl methacrylate (Laporte)

**ADEKA Reasoap SR-10** – (Asahi Denka)

**ADEKA Reasoap ER20**– (Asahi Denka)

**ADEKA Reasoap ER30**– (Asahi Denka)

**Mono&Di&Tri&Highly functional monomer and oligomer acrylate** (Cray Vally)

**Marlon AS** – Alkylbenzene sulphonic acid (Condea)



Marlon A - Alkylbenzene sulphonate sodium salt (Condea)

DISPONIL FES 32 - Fatty alcohol poly glycole ether sulphate, sodium salt

Disponil AES 72 - Alkyl Aryl Polyglycole ether Sulphate sodium salt

**Biocides:**

**Acticide SPX-** 5-chloro-2-methyl-2H-isothiazol-3-one + methyl - 2H - isothiazol - 3 - one (THOR).

**Acticide GR** - 2,2',2''-(hexahydro-1,3,5-triazine-1,3,5-triyl)triethanol (THOR)  
(May be Mergal KM200 of Troy).

**Acticide MBS** - Combination of 1,2-benzisothiazol-3(2H)-one + 2-methyl-2H-isothiazol-3-one (THOR)

**Acticide FS** - methylisothiazolones and Formaldehyde donors(THOR)

**Nipacide OPG-** N-octylisothiazolinone (Nipa Laboratories)

**Rheological Modifiers:**

**Carbopol 846** -(BFGoodrich)

**Prox AM162** - Aqueous emulsion of an acrylic copolymer (Synthron)

**Commercial Monomers:**

Acrylamide - (Cytecs, Stan Chem)

Acrylic Acid - (Atochem)

Acrylonitrile - (DSM)

Butyl Acrylate - (Rohm&Haas, Basf, Atochem)

Ethyl Acrylate - (Rohm&Haas, Basf, Atochem)

2 - Ethyl Hexyl Acrylate - (Hoechst, Nippon, Basf)

Methyl Methacrylate - (Deggusa, Basf, Atochem)

Styrene - (Gadot)

**EXAMPLES**

In all the following examples, where addition of AO is not described, it may be added to the final dispersion with short mixing.

**Example 1:**

This example shows how to obtain a copolymer of PBBMA, acrylic acid, N-methylol acryl amide, acrylo nitrile, butyl acrylate, and methyl methacrylate. Such a copolymer was obtained according to this example, and was found to include 32% (w/w) bromine. The aqueous solution obtained in accordance with this example had a 45% solids content with typical particle size of 475nm and viscosity of 3580cps (Brookfield, LVT, spindle 3, 12 rpm).

In this example the aqueous polymeric dispersion is obtained from a PBBMA dispersion and an emulsion of the other monomers. Monomers and polymerizing agents are fed simultaneously.

Preparation of the PBBMA dispersion: To a 2-liter round bottom flask, fitted with mechanical stirrer, add 450gr water and about 150-200gr of diluted dispersing agents. The dispersing agents should be a combination of an anionic surfactant and a non-ionic surfactant in weight ratio of 1:1. The non-ionic surfactant is to be an alkyl phenol based dispersing agent with a Low HLB, of about 7-11.

After short mixing an emulsion is obtained. Add slowly to the emulsion, 400gr of commercial PBBMA powder (FR1025M, average particle size of 5-8 micron), and 1gr biocide (in this order). The obtained dispersion should then be mixed for another 10 minutes.

Grind the dispersion until the particle size is about 600-1500nm. This may be done with High Sheer Homogenizer, such as IKA Ultraturax T-50, operated for about 20 minutes followed by additional 3 cycles of grinding process with pearl mill such as Dyno mill, to obtain the required size. All grinding should be carried out while temperature is observed not to raise over 30°C. After grinding, PH

should be adjusted to 7-8.

Pre-emulsion: To a 1 liter round bottom flask, fitted with mechanical stirrer, add about 70gr water and 3-8gr of anionic surfactant. After 5-10 min stirring at about 250rpm, add slowly, one by one, and with continuous stirring, the following ingredients: 2-6gr acrylic acid, 15-40gr N-methylol acryl amide (45% solids), 15-30gr acrylonitrile, 80-110gr butyl acrylate, 40-70gr methyl methacrylate and about 15gr water. The obtained pre emulsion should be mixed for another 15 minutes.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, 2 dropping funnels and Nitrogen inlet, add about 120gr water, 0.5gr sodium bicarbonate and 0.5gr sodium carbonate. Hot water should be passed through the jacket, to warm the solution up to 80-82°C. Continuous stirring (200-300rpm) should be applied. Nitrogen is to be introduced under the surface of the liquid for about 10 min. First initiator solution, made by dissolving 0.5gr APS in 5gr water, is then added. 5 min later, 10-20gr of the pre-emulsion described above is to be added. Few minutes later, when no change in Temp is observe, the rest of pre emulsion is to be slowly added through one dropping funnel (this should take about 3.5 hours). 500gr of the PBBMA dispersion described above should then be added, through the second dropping funnel, drop wise. This takes about 1.5 hours. A main initiator solution, prepared by dissolving 1.8-3gr APS and 1gr ammonia in 40gr water is added through a separate dropping funnel, during both pre emulsion and dispersion addition. Temperature should be kept at 80-82°C during the entire procedure. About 4 hours from the beginning of the polymerization, raise the temperature to 85°C, and stir the dispersion obtained for another 45-55 min. Lower the temperature to 65°C, and add a solution of 1.4gr TBHP in 4gr water. After 5 min, add a solution of 0.9gr Formosul in 8gr water, cool the dispersion to room temperature, and add 2gr Ammonia, 10-20gr of dispersing agent and about 3gr biocide with constant

stirring. The dispersing agent should be of the alkyl phenol type, with HLB value of between about 13.

**Example 2:**

In this example, obtained is a copolymer of PBBMA, acrylic acid, N-methylol acryl amide, and butyl acrylate. Aqueous dispersions obtained in accordance with this examples had about 46-47% solid content, where the solids are 32% bromine. In two repetitions the particle sized varied from 134 to 154nm, and with it the viscosity changed from 1580 to 3060cps (Brookfield, LVT, spindle 3, 12 rpm).

A textile impregnated with this dispersion (after addition of the antimony penta-oxide dispersion) to a pick up of 25.8% was found to be fire retardant in accordance with the standard cited above. Antimony penta-oxide was added in the form of dispersion, sold under the trade name NyacolA1550, in concentration of 18.5gr per 100gr polymeric dispersion

Here, a pre-dispersion of PBBMA with the other monomers is first prepared from the PBBMA dispersion described above, mixed with the other monomers and suitable surface active agents, and then this pre-dispersion is polymerized.

Pre-dispersion: To a 1 liter round bottom flask, fitted with mechanical stirrer, 500gr of the described PBBMA dispersion is added together with 3-8gr of surfactant combination, made of two surfactants, one being anionic, and the other non-ionic with high HLB of about 14-18. The weight ration between the anionic and non-ionic surfactants should be 2:1. Also added to the dispersion, slowly, with continuous stirring, and in the following order are 1-5gr acrylic acid, 15-40gr N-methylol acryl amide (45% solids), 165-200gr butyl acrylate and 15gr water. This leads to the formation of a stable pre dispersion that should be stirred for another 15 minutes.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with

warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, dropping funnel and Nitrogen inlet, one should add 220gr water, 0.05-0.5gr of the non-ionic surfactant used in the combination mentioned above, and 0.5gr Ammonia. Hot water is to be passed through the jacket, to warm the solution up to 80-82°C. Continuous stirring (200-300rpm) should be applied. Nitrogen is introduced under the surface of the liquid for 10 min. First initiator solution, made by dissolving 0.5gr APS in 5gr water, is to be added, and 5 minutes later, the pre emulsion is to be added through the dropping funnel, drop wise, over 4 hours. Main initiator solution, prepared by dissolving 1-3gr APS and 0.5gr ammonia in 40gr water is added as well, simultaneously with the pre dispersion. Temperature should be kept at 80-82°C during the procedure. After 4 hours, temperature is to be allowed to raise to 85°C, and the dispersion is stirred for another 45-55 minutes. The temperature is then lowered to 65°C, and solution of 0.5gr TBHP in 5gr water is added. After 5 min, solution of 0.3-2gr Formosul in 5gr water is added. The dispersion is cooled to room temperature, and 0.5gr anti-foam and 2gr biocide should be added with stirring.

### **Example 3:**

This example teaches how to obtain a copolymer of the same monomers as in Example 2, however, in the present example, the dispersion obtained has somewhat lower solid content of 41%, and significantly lower viscosity, of only 62cps (Brookfield, LVT, spindle 1, 60rpm). The particle size was measured to be 116nm and the bromine content was 30.6%.

This example uses a PBBMA dispersion as described under example 1 above, and a pre-emulsion with the other monomers. The dispersion, pre-emulsion and main initiator were added all simultaneously.

Pre-emulsion: To a 1 liter round bottom flask, fitted with mechanical stirrer, add

130gr water and 1-5gr of a surfactant combination. This combination is like the one used in example 2, but the weight ratio between the anionic and non-ionic surfactants is 4:1, rather than 2:1 used in example 2. After 5-10 min stirring at 250rpm add slowly, with continuous stirring, and in the following order: 1-5gr acrylic acid, 15-40gr N-methylol acryl amide (45% solids), 140-170gr butyl acrylate and 15gr water. The stable pre emulsion thus obtained is to be stirred for additional 15 minutes.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, 2 dropping funnels and Nitrogen inlet, add 168gr water, and 0.5gr Ammonia. Hot water should be passed through the jacket, to warm the solution up to 80-82°C. Apply continuous stirring (200-300rpm). Introduce nitrogen under the surface of the liquid for 10 min. Add a first initiator solution, made by dissolving 0.5gr APS in 3gr water. After 5 minutes add the pre emulsion through one dropping funnel and 440gr of PBBMA dispersion, described above, through the second dropping funnel. Add the dispersion and pre-emulsion simultaneously drop wise, over 4 hour. Prepare a main initiator solution by dissolving 1-3gr APS and 0.5gr ammonia in 40gr water, and add them as well, simultaneously with both dispersion and pre emulsion. Temperature must be kept at 80-82°C during the procedure. After 4 hours, temperature should be raised to 85°C, and the dispersion stirred for another 45-55 min. The temperature should then be lowered to 65°C, and solution of 1-3gr TBHP in 5gr water be added. After 5 min, add solution of 0.3-2gr Formosul in 5gr water. Cool the thus obtained dispersion to room temperature, and add with stirring 2gr Ammonia and 2gr biocide.

#### **Example 4:**

Preparation of copolymer of PBBMA, butyl acrylate and acrylic acid. The example allows obtaining a polymeric aqueous dispersion with a solids content

of about 40% and bromine content of about 52%, which is also characterized by exceptionally small particle size of 87nm, with exceptionally low viscosity of 12cps (Brookfield, LVT, spindle 1, 60 rpm).

PBBMA dispersion: To a 2-liter round bottom flask, fitted with mechanical stirrer, add 450gr water and 50-80gr of a dispersing agents combination. This combination should be a 1:1 combination of an anionic and nonionic surfactant. After short mixing, add slowly about 480gr of commercial PBBMA powder (FR1025M, average particle size of 5-8 micron) and follow it by adding 1gr biocide. Mix the obtained dispersion for another 10 minutes. Grind the dispersion with High Sheer Homogenizer such as IKA Ultraturax T-50, for 20 min while keeping temp max 30°C. Transfer the dispersion for additional 3 cycles of grinding with pearl mill, such as Dyno mill, until having particle size of 600-1500 nm. Adjust the PH to 7-8.

Solution: To a 1 liter round bottom flask, fitted with mechanical stirrer, add slowly, one by one in the given order 50-100gr butyl acrylate, 1-5gr acrylic acid and 1-5gr of an alkyl aryl sulphonic acid.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, 2 dropping funnels and Nitrogen inlet, add 140gr water, 1gr of a nonionic high HLB alkyl phenol based surfactant and 0.6gr Ammonia. Hot water should be passed through the jacket, to warm the solution up to 80-82°C. Continuous stirring at 200-300rpm should be applied. Introduce nitrogen under the surface of the liquid for 10 min, and then add a first initiator solution, made by dissolving 0.5gr APS in 3gr water. 5 min later, add drop wise, over 5 hours, the solution through one dropping funnel simultaneously with adding through the second dropping funnel a mixture of 700gr of the PBBMA dispersion described above and 15-40gr N-Methylol Acryl Amide. Still simultaneously, add a main initiator solution, prepared by dissolving 1.5gr APS, 1-3gr nonionic high

HLB alkyl phenol based surfactant and 0.5gr ammonia in 30gr water. Temperature should be kept at 80-82°C during the procedure. After 5 hours, temperature should be raised to 85°C, and the dispersion should be mixed for another 45-55 min. The temperature is then lowered to 65°C, and solution of 0.5gr TBHP in 5gr water is added. After 5 min, solution of 0.35gr Formosul in 5gr water is added. The dispersion is then let to cool to room temperature, and 0.5gr antifoam and 2 gr biocide are to be added while stirring.

**Example 5:**

Preparation of copolymer of PBBMA, butyl acrylate, 2-ethyl hexyl acrylate and acrylic acid. The example allows obtaining a polymeric aqueous dispersion with a solids content of about 46% and bromine content of 20%, which is also characterized by low Tg value of -12°C (calculated), particle size of 186nm, with viscosity of 860cps (Brookfield, LVT, spindle 3, 12 rpm).

PBBMA dispersion: To a 2-liter round bottom flask, fitted with mechanical stirrer, add 360gr water and 40-55gr of a 1:1 combination of low HLB alkyl phenol based nonionic dispersing agent and anionic surfactant. After short stirring, add slowly 490gr of commercial PBBMA powder (FR1025M, average particle size of 5-8 micron) and 8gr antifoam, followed by 1gr biocide. Stir the obtained dispersion for another 10 minutes. Grind the obtained dispersion with High Sheer Homogenizer, such as IKA Ultraturax T-50 for 20 minutes while keeping the temp at maximum 30°C. Transfer the ground dispersion for 3 additional grinding cycles with pearl mill (Dyno mill), until a particle size of 600-1500 nm is obtained. Adjust the PH to 7-8.

Pre-dispersion: To a 1 liter round bottom flask, fitted with mechanical stirrer, add 3-8gr of surfactant combination, made of two alkyl phenol based surfactants, one being anionic, and the other non-ionic with high HLB of about 14-18. The weight



ration between the anionic and non-ionic surfactants should be 2:1. Also add to the dispersion, slowly, with continuous stirring, and in the following order 1-5gr acrylic acid, 15-40gr N-methylol acryl amide (45% solids), 140-200gr butyl acrylate, 140-200 gr 2 ethyl hexyl acrylate and 15gr water. This leads to the formation of a stable predispersion, that should be stirred for another 15 minutes.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, 2 dropping funnels and Nitrogen inlet, add 202gr water, 0.05-2gr of a nonionic high HLB alkyl phenol based surfactant and 0.5gr Ammonia. Hot water should be passed through the jacket, to warm the solution up to 80-82°C. Continuous stirring at 200-300rpm should be applied. Introduce nitrogen under the surface of the liquid for 10 min, and then add a first initiator solution, made by dissolving 0.5gr APS in 3gr water. 5 min later, add drop wise, over 5 hours, the pre dispersion through one dropping funnel simultaneously with adding through the second dropping funnel 265 gr of the PBBMA dispersion described above. Still simultaneously, add a main initiator solution, prepared by dissolving 1-3gr APS and 0.5gr ammonia in 40gr water. Temperature should be kept at 80-82°C during the procedure. After 5 hours, temperature should be raised to 85°C, and the dispersion should be mixed for another 45-55 min. The temperature is then lowered to 65°C, and solution of 1-3gr TBHP in 5gr water is added. After 5 min, solution of 0.3-2gr Formosul in 5gr water is added. The dispersion is then let to cool to room temperature, and 0.5gr antifoam and 2 gr biocide are to be added while stirring.

#### **Example 6:**

A PBBMA-alkyl methacrylate copolymer with 68% bromine, viscosity of 20 cps, solid content of 41.5% and particle size of 100nm.

PBBMA dispersion: Prepare as in the previous example.

Prepare a solution by dissolving 2-8 gr of low HLB nonionic dispersing agent, the same weight of anionic surfactant and 1-4 gr thickening agent in 100gr Water.

Prepare a semi-final PBBMA dispersion by mixing the above dispersion and solution in 9:1 w/w proportions.

Final Dispersion: To a 1 liter round bottom flask, fitted with mechanical stirrer, add slowly, with continuous stirring, 800gr of the above semi-final PBBMA dispersion and 0.05-3 gr Allyl Methacrylate.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, dropping funnels and Nitrogen inlet, add 130gr water, 1-4gr high HLB nonionic surfactant and 0.6gr Ammonia. Let hot water pass through the jacket, to warm the solution up to 80-82°C with continuous stirring at 200-300rpm. Introduce nitrogen under the surface of the liquid for 10 min. Five minutes later add a first initiator solution, made by dissolving 0.5gr APS in 3gr water. Another 5 min later, add the final dispersion through the dropping funnel, drop wise, over 4.5 hour. Add a main initiator solution, prepared by dissolving 1-3gr APS, 0.1-2gr high HLB nonionic surfactant and 0.5gr ammonia in 30gr water simultaneously with adding both the dispersion and pre emulsion. Keep temperature at 80-82°C during the procedure. After 4.5 hours, raise the temperature to 85°C, and mix the dispersion for another 45-55 min. Let the temperature cool to 65°C, and add a solution of 1-3gr TBHP in 5gr water. After 5 min, add a solution of 0.3-2gr Formosul in 5gr water. Let the dispersion cool to room temperature, and add with stirring 0.5gr antifoam and 2gr biocide.

#### **Example 7:**

Another recipe for a copolymer and aqueous dispersion containing it is given in the present example. The polymer obtained by the inventor in accordance with

this example contained 50.6% solids, and had a viscosity of 16200cps (Brookfield, LVT, spindle 4, 12 rpm). The polymer particle size was measured to be 134nm, and the bromine content was 26.8%.

The polymeric dispersion was applied over various kinds of fabrics, including cotton and polyester. The treated fabrics were tested according to test CFR16/1615. The results were good, such the the treated fabrics may be considered as sufficient flame retarded in accordance with said test.

PBBMA dispersion: The same as in Example 1.

Pre-emulsion: To a 1 liter round bottom flask, fitted with mechanical stirrer, add 90gr water and 5-9gr Anionic surfactant. After 5-10 min mixing at 250rpm, add slowly, one by one and while stirring the following ingredients: 1-3gr acrylic acid, 25-40gr N-methylol acryl amide (45% solids), 220-290gr butyl acrylate and 15gr water. Stir the thus obtained stable pre emulsion for another 15 min.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, 2 dropping funnels and Nitrogen inlet, add 90gr water, 0.5-3gr Anionic surfactant and 0.5gr Ammonia. Pass hot water through the jacket, to warm the solution up to 80-82°C. Apply Continuous stirring at 200-300rpm. Introduce nitrogen under the surface of the liquid for 10 min. Add a first initiator solution, made by dissolving 0.5gr APS in 3gr water. 5 min later, add 8-25 gr of the pre-emulsion described above. Few minutes later, when no change in Temp is observed, add the rest of the pre emulsion through one dropping funnel and through the second dropping funnel add 472gr of the PBBMA dispersion of example 1, drop wise, over 4 hour. Add a main initiator solution, prepared by dissolving 1-3gr APS and 0.5gr ammonia in 40gr water simultaneously with the dispersion and the pre emulsion. Keep Temperature at 80-82°C during the procedure. After 4 hours, raise temperature to 85°C, and mix the obtained dispersion for another 45-55 min. Let the temperature drop to 65°C, and add a

solution of 1-3gr TBHP in 5gr water. After 5 min stirring, add a solution of 0.3-2gr Formosul in 5gr water. Cool the obtained dispersion to room temperature, and add with stirring 2gr Ammonia and 2gr Biocide.

**Example 8:**

This is another example for an extraordinary non-viscous dispersion obtainable in accordance with the present invention. This polymeric dispersion was applied to various kinds of fabrics, such as cotton and polyester, and tested according to test CFR16/1615. The results were good, such that the treated fabrics may be considered as sufficient flame retarded.

The aqueous dispersion prepared by the inventor in accordance with the present example had 40.1% solid content and a viscosity as low as 10cps (Brookfield, LVT, spindle 1, 60 rpm). The polymer particle size was measured to be 137nm, and the polymer bromine content was 43%.

PBBMA dispersion: The same as in Example 4.

Pre-emulsion: To a 1 liter round bottom flask, fitted with mechanical stirrer, add 90gr water, 5-8gr of a 2:1 mixture of Anionic surfactant and with Nonionic high HLB surfactant. After 5-10 min mixing at 250rpm, add slowly, with constant stirring according to the following order 1-4gr acrylic acid, 15-30gr N-methylol acryl amide (45% solids), 110-150gr butyl acrylate and 15gr water. Stir the stable pre emulsion thus obtained for another 15 min.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, 2 dropping funnels and Nitrogen inlet, add 177gr water, and 0.55gr Ammonia. Pass hot water through the jacket to warm the solution up to 80-82°C. Apply Continuous stirring at 200-300rpm. Introduce nitrogen under the surface of the liquid for 10 min. Add a first initiator solution, made by dissolving 0.5gr APS in 3gr water. 5 min later, add the pre emulsion one of the

dropping funnels and 492gr of PBBMA dispersion of example 4 through the other dropping funnel, drop wise, over 5 hours. Add a main initiator solution, prepared by dissolving 1-3gr APS and 0.5gr ammonia in 40gr water simultaneously with both dispersion and pre emulsion. Keep temperature at 80-82°C during the procedure. After 5 hours, raise the temperature to 85°C, and stir the dispersion for another 45-55 min. Lower the temperature to 65°C, and add a solution of 1-3gr TBHP in 5gr water. After 5 min, add a solution of 0.3-2gr Formosul in 5gr water. Cool the obtained dispersion to room temperature, and add with stirring 2gr Antifoam and 2 gr Biocide.

**Example 9:**

Here a copolymer of PBBMA, butyl acrylate, acrylic acid and N-methylol acryl amide is prepared. The inventor obtained in accordance with this example, an aqueous polymeric dispersion having 49.3% solid content and viscosity of 530cps (Brookfield, LVT, spindle 2, 30 rpm). The polymer was measured to have a particle size of 176nm and bromine content of 47.2%. This polymeric aqueous dispersion was applied to various kinds of fabrics, such as cotton, polyester, etc, and tested according to test CFR16/1615. The results were good, such that the treated fabrics may be considered as sufficient flame retarded.

PBBMA dispersion: The same as in Example 4.

Solution: To a 1 liter round bottom flask, fitted with mechanical stirrer, add slowly, with constant mixing, by the given order, 60gr butyl acrylate, 1-3gr Acrylic Acid and 0.5-1.5 anionic alkyl aryl solphonic acid based surfactant slowly.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, 2 dropping funnels and Nitrogen inlet, add 134gr water, 1-4gr nonionic high HLB surfactant and 0.6gr Ammonia. Pass hot water through

the jacket, to warm the solution up to 80-82°C. Stir continuously at 200-300rpm. Introduce nitrogen under the surface of the liquid for 10 minutes. Add a first initiator solution, made by dissolving 0.5gr APS in 3gr water. 5 min later, add the obtained solution through one dropping funnel, and add simultaneously through the other dropping funnel, drop wise, over 5 hours, a mixture of 660gr of final PBBMA dispersion, described under example 4, and 25-40gr N-Methylol Acryl Amide. Add a main initiator solution, prepared by dissolving 1-3gr APS, 0.5-2gr nonionic high HLB surfactant and 0.5gr ammonia in 30gr water, simultaneously with both the dispersion and the pre emulsion. Keep the temperature at 80-82°C during the procedure. After 5 hours, raise the temperature to 85°C, and stir the obtained for another 45-55 min. Lower the temperature to 65°C, and add a solution of 1-3gr TBHP in 5gr water. After 5 min, add a solution of 0.3-2gr Formosul in 5gr water. Cool the dispersion to room temperature, and add with stirring 0.5gr Antifoam and 2gr Biocide.

**Example 10:**

This and the following two examples demonstrate another aspect of the present invention, according to which a solution (rather than dispersion or emulsion) of the brominated polymer is first prepared.

In accordance with this example an aqueous dispersion with 48% solid content, and viscosity of 15cps (Brookfield, LVT, spindle 1, 60 rpm) was prepared. The polymer included therein was made of PBBMA, acrylic acid and N-methylol acryl amide, had a bromine content of 24.3% and the size of the polymeric particles was 950nm. The obtained polymer had a calculated Tg of 115°C.

PBBMA solution: To a 1 liter round bottom flask, fitted with mechanical stirrer, add 320-350 gr styrene and warm up to 45-50°C. Add 130-180PBBMA powder (styrene: PBBMA weight ratio 1.8:1) and stir until the obtained solution appears to be clear. Cool the solution to room temperature.

Pre-emulsion: To a 1 liter round bottom flask, fitted with mechanical stirrer, add

204gr water, 1-4gr linear anionic surfactant, 3-6gr non ionic, alcohol Ethoxylated surfactant with HLB value of 15-18, 3-6gr acrylic acid, 15-30gr N-methylol acryl amide (45% solids), the above PBBMA solution and 15 gr water. These ingredients should be added slowly, in the given order, with continuous stirring. Stir the stable pre emulsion obtained in this manner for another 15 min.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, dropping funnel and Nitrogen inlet, add 204gr water, 0.5 gr sodium carbonate and 0.5gr sodium bicarbonate. Pass hot water through the jacket, to warm the solution up to 80-82°C. Stir continuously at 200-300rpm. Introduce nitrogen under the surface of the liquid for 10 minutes. Add a first initiator solution, made by dissolving 0.5gr APS in 5gr water. 5 min later, add the pre emulsion obtained this way through the dropping funnel, drop wise, over 4 hours. Add a main initiator solution, prepared by dissolving 1-3gr APS and 1gr ammonia in 40gr water simultaneously with adding the pre emulsion. Keep the temperature at 80-82°C during the procedure. After 4 hours, raise the temperature to 86°C, and stir the obtained dispersion for another 45-55 min. Lower the temperature to 70°C, and add a solution of 1-3gr TBHP in 4gr water. After 5 min, add a solution of 0.5-2gr Formosul in 8gr water. Cool the obtained dispersion to room temperature, and add 2gr Ammonia and 2gr biocide while stirring.

A polymer obtained in accordance with this example was applied to various kinds of fabrics such as cotton and polyester, and tested according to test CFR16/1615. The results were good and the substrates may be considered as sufficient flame retarded.

#### **Example 11:**

The polymer obtained in the present example is similar in monomer content to that obtained in the preceding example, but includes also butyl acrylate, which

makes it more hydrophobic and lowers its Tg value.. Please note also the difference in the order according to which the components are added to the pre-emulsion. The aqueous dispersion obtained in accordance with this example had 50.8% solids content and viscosity of 31cps (Brookfield, LVT, spindle 1, 60 rpm). The polymer had a particle size of 803nm and bromine content of 20.5%. The calculated Tg of the obtained polymer was 59C.

PBBMA solution: Prepare according to Example 10.

Pre-emulsion: To a 1 liter round bottom flask, fitted with mechanical stirrer, add slowly, with stirring and by the following order 204gr water, 1-4gr linear anionic surfactant, 3-6gr non ionic, high HLB alcohol Ethoxylated surfactant, 3-6gr acrylic acid, 15-30gr N-methylol acryl amide (45% solids), 120-160gr butyl acrylate, the above PBBMA solution and 15 gr water. Stir the stable pre emulsion obtained this way for another 15 min.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, dropping funnel and Nitrogen inlet, add 180gr water, 0.6gr ammonia and 1gr sodium bicarbonate. Pass hot water through the jacket, to warm the solution up to 80-82°C. Stir Continuously at 200-300rpm. Introduce nitrogen under the surface of the liquid for 10 minutes. Add a first initiator solution, made by dissolving 0.5gr APS in 5gr water. 5 min later, add the pre emulsion through the dropping funnel, drop wise, over 4 hours. Add also a main initiator solution, prepared by dissolving 1.7-2.7gr APS and 1gr ammonia in 40gr water, simultaneously with adding the pre emulsion. Keep the temperature at 80-82°C during the procedure. After 4 hours. Raise the temperature to 86°C, and stir the dispersion for another 45-55 min. Lower the temperature to 70°C, and add a solution of 1-3gr TBHP in 4gr water. After 5 min, add a solution of 0.5-2gr Formosul in 8gr water. Cool the dispersion to room temperature, and add with stirring 2gr Ammonia and 2gr biocide.



**Example 12:**

This example shows that antimony oxide may be added to the aqueous dispersion during the polymerization process, and it may also be added into the pre-emulsion before polymerization.

A polymer that was prepared in accordance with the present invention had 51.9% solid content, and viscosity of 2250cps (Brookfield, LVT, spindle 4, 12 rpm). The polymer showed particle size of 138nm, bromine content of 22.5%, and had a calculated Tg of 116°C.

PBBMA solution: Prepare as detailed in Example 10.

Pre-emulsion: To a 1 liter round bottom flask, fitted with mechanical stirrer, add slowly, one by one, in accordance with the given order, and with constant stirring 204gr water, 3-6gr anionic surfactant, 1-4gr acrylic acid, 20-35gr N-methylol acryl amide (45% solids), 75-90gr antimony pentaoxide dispersion(Nyacole A1550PH7) the above PBBMA solution and 15gr water. Stir the stable pre emulsion thus obtained for another 15 minutes.

Polymerization process: To a 1.7 liter, 5-neck, round bottom flask, with warming/cooling double glassing jacket, fitted with mechanical stirrer, reflux condenser, thermometer, dropping funnel and Nitrogen inlet, add 122gr water, 75-90gr antimony pentaoxide dispersion (Nyacole A1550PH7), 0.5-3 gr anionic surfactant and 0.5gr sodium bicarbonate. Pass hot water through the jacket, to warm the solution up to 80-82°C. Stir continuously at 200-300rpm. Introduce nitrogen under the surface of the liquid for 10 min. Add a first initiator solution, made by dissolving 0.4gr APS in 5gr water. 5 minutes later, add the pre emulsion through the dropping funnel, drop wise, over 4 hours. Add a main initiator solution, prepared by dissolving 1-3gr APS and 1gr ammonia in 35gr water simultaneously with the addition of the pre emulsion. Keep the temperature at 80-82°C during the procedure. After 4 hours, raise the temperature to 86°C, and stir the dispersion for another 45-55 min. Lower the temperature to 70°C, and

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add a solution of 1-3gr TBHP in 4gr water. After 5 min, add a solution of 0.5-2gr Formosul in 8gr water. Cool the obtained dispersion to room temperature, and add 2gr Ammonia and 2gr biocide while stirring.

**CLAIMS:**

1. A polymer made of (i) at least one non-brominated monomer and (ii) at least one brominated monomer having the structure A-B-C, wherein A is a phenyl, substituted with 3-5 bromine atoms, B is a C<sub>1</sub> to C<sub>4</sub> alkyl, optionally substituted with 1 to 8 bromine atoms, and C is an acrylic or methacrylic group, said polymer being characterized in having bromine contents of 20%(w/w) or more.
2. A polymer according to claim 1, wherein said phenyl is substituted with 5 bromine atoms.
3. A polymer according to claim 1, wherein said alkyl is CH<sub>2</sub>.
4. A polymer according to claim 1, wherein said acrylic group is acrylate.
5. A polymer according to claim 1, wherein said brominated monomer is penta bromo benzyl acrylate (PBBMA).
6. A polymer according to claim 1 wherein said bromine contents is 60-70%.
7. A polymer according to claim 1, wherein said bromine content is 25 - 50%.
8. A polymer according to claim 1, wherein said bromine content is 20 - 35%.
9. A polymer according to any one of the preceding claims, having a non-brominated monomer that is a specialty monomer.
10. A polymer according to the preceding claim, wherein said specialty monomer is selected from monomers that are cross-linking, surface active, and/or adhesion promoting.
11. A polymer according to claim 9 wherein said specialty monomer is selected from sodium salt of 2-acrylamido-2-methyl propane sulphonic acid, betal-carboxymethyl acrylate, ammonium allyloxypolyethoxy(10)sulphate, laurethoxy(23)methacrylate, laurethoxy(25)methacrylate, allyl methacrylate, and hydroxyl ethyl methacrylate, glycidyl methacrylate, ammonium salt of  $\alpha$ -sulfo- $\omega$ -[1-(Alkoxy)methyl-2-(2-propenyloxy)ethoxy]- $\omega$ -hydro-poly(oxy-1,2,-ethanediyl), ammonium salt of  $\alpha$ -[1-(Alkoxy)methyl-2-(2-propenyloxy)ethoxy]- $\omega$ -hydro-poly(oxy-1,2,-ethanediyl), ditrimethylo propane tetraacrylate, ethoxilated trimetholopropabe triacrylate, and trimethylo propabe acrylate.

12. A polymer according to any one of claims 1 to 8, having a non-brominated monomer selected from the group consisting of acrylic monomers, vinyl acetate and styrene or a styrene derivative.
13. A polymer according to the preceding claim, wherein said acrylic monomer is selected from acrylamide, acrylic acid, acrylonitrile, butyl acrylate, ethyl acrylate, 2-ethyl hexyl acrylate, and methyl methacrylate.
14. A polymer according to any one of claims 1-8, having a non-brominated monomer of the formula  $R_1CH=CR_2C(O)A$ , wherein
  - A is selected from the group consisting of  $OR_3$ ,  $NR_3R_4$ , and  $CN$ ; and
  - $R_1$  and  $R_2$  are each independently selected from H and alkyl, said alkyl being linear or branched, and each of  $R_3$  and  $R_4$  independently may be H, alkyl, alkenyl, alkoxy, polyalkoxy, alkanol, or ether, each of which may be linear or branched, substituted or unsubstituted.
15. A polymer according to the preceding claim, wherein the carbon-containing R groups have between 1 and 15 carbons.
16. A polymer according to the preceding claim, wherein the alkyl groups have between 1 and 4 carbon atoms.
17. A polymer according to any one of the preceding claims, having a Tg of less than 0°C.
18. A mixture comprising a polymer according to any one of the preceding claims and more than one surface active agent.
19. A mixture according to the preceding claim, further containing antimony oxide.
20. An aqueous dispersion comprising a polymer made of a bromine-containing monomer having the structure A-B-C, wherein A is a phenyl, substituted with 3-5 bromine atoms, B is a  $C_1$  to  $C_4$  alkyl, optionally substituted with one to 8 bromine atoms, and C is an acrylic or methacrylic group and at least one non-brominated monomer, characterized in that said dispersion has a solid content of at least 40%.
21. An aqueous dispersion according to claim 20, wherein said phenyl is substituted with 5 bromine atoms.
22. An aqueous dispersion according to claim 20 or 21 wherein said alkyl is  $CH_2$ .

23. An aqueous dispersion according to claim 20 wherein said brominated monomer is PBBMA.
24. An aqueous dispersion according to claim 20, wherein said polymer is according to any one of claims 1 to 17.
25. An aqueous dispersion according to any one of claims 20 to 24, further comprising at least two different surface active agents.
26. An aqueous dispersion according to the preceding claim, wherein one or more of said surface active agents is an alkyl aryl.
27. An aqueous dispersion according to any one of claims 20 to 26, further containing antimony oxide.
28. An aqueous dispersion according to any one of claims 20 to 27, consisting essentially of solid particles in aqueous solution, wherein the size of said solid particles is less than 2000nm.
29. An aqueous dispersion according to the preceding claim, wherein said size is between 50 and 1000nm.
30. An aqueous dispersion according to the preceding claim, wherein said size is between 80 and 400nm.
31. An aqueous dispersion according to any one of claims 20 to 30, wherein said polymer has a density of 1.2g/cc or more.
32. An aqueous dispersion according to any one of claims 19 to 30, wherein said polymer has a molecular weight of 500,000 and above.
33. An aqueous dispersion according to the preceding claim, wherein said polymer has a molecular weight of 1,000,000 or above.
34. An aqueous dispersion according to any one of claims 20 to 33, which is stable for at least six months in -7-35°C with no direct sunlight.
35. An aqueous dispersion according to any one of claims 20 to 33, which is stable for at least six months in 5 to 35°C with no direct sunlight.
36. A product comprising antimony oxide and a polymer made of at least one bromine-containing monomer and at least one non-brominated monomer, wherein said product is fire-retardant.

37. A product according to claim 36, wherein said polymer is according to any one of claims 1 to 17.
38. A product according to claim 36 or 37, comprising a textile, said textile being printed, sprayed, or impregnated with an aqueous dispersion according to any one of claims 27-35.
39. A product according to claim 38, wherein said non-brominated monomer is hydrophobic.
40. A product according to claim 39, wherein said hydrophobic monomer is selected from the group consisting of butyl Acrylate, 2-ethyl hexyl acrylate, styrene, and styrene derivatives.
41. A method for fabricating a fire-retardant textile, comprising printing, spraying or impregnating a textile with an aqueous dispersion, which is according to any one of claims 20-35.
42. A method for improving the hydrophobicity of a textile, comprising printing, spraying, or impregnating said textile with an aqueous dispersion according to any one of claims 20 to 35.
43. A method according to the preceding claim, wherein the polymer dispersed in said dispersion includes a hydrophobic non-brominated monomer.
44. A method according to claim 41, wherein said hydrophobic non-brominated monomer is selected from the group consisting of butyl Acrylate, 2-ethyl hexyl acrylate, and styrene.
45. A method for obtaining an aqueous dispersion of a co-polymer containing at least a first monomer and a second monomer, wherein said second monomer is at least partially dissolved in said first monomer, and reacts to polymerize therewith in the presence of water and surfactants; said method being characterized in that said first monomer is a brominated aromatic compound.
46. A method according to the preceding claim, wherein said brominated aromatic compound has the structure A-B-C, wherein A is a phenyl, substituted with 3-5 bromine atoms, B is a C<sub>1</sub> to C<sub>4</sub> alkyl, optionally substituted with one to 8 bromine atoms, and C is an acrylic or methacrylic group.

47. A method according to claim 45 or 46 wherein the phenyl in said first monomer is substituted with 5 bromine atoms.
48. A method according to claim 45 or 46, wherein the alkyl in said first monomer is  $\text{CH}_2$ .
49. A method according to the preceding claim, wherein said first monomer is PBBMA.
50. A method according to claim 45, wherein said first monomer is a bromostyrene or a derivative thereof.
51. A method according to any one of claims 45 to 50, wherein said second monomer is styrene or a styrene derivative.
52. A method according to any one of claims 45 to 51 wherein the amount of said water is such that the obtained dispersion has at least 40% solid content.
53. A method according to any one of claims 45 to 52, wherein the ratio between said first monomer and non-brominated monomers is such that the obtained polymer has at least 20%(w/w) bromine content.
54. A method according to any one of claims 45 to 53, wherein at least one of said surfactants is reactive, and the obtained polymer contains said first monomer, said second monomer, and said reactive surfactant.
55. A method according to any one of claims 45 to 54, wherein said first and second monomer react with at least one other monomer, such that the polymer obtained by the method is of said first monomer, said second monomer, and said at least one other monomer.
56. A method according to the preceding claim, wherein said at least one other monomer is a specialty monomer.
57. A method according to the preceding claim, wherein said specialty monomer is selected from monomers that are cross-linking, surface active, and adhesion promoting.
58. A method according to claim 56 or 57 wherein said specialty monomer is selected from the group consisting of N-(Hydroxymethyl)acrylamide, sodium salt of 2-acrylamido-2-methyl propane sulphonic acid, betal-carboxymethyl acrylate,

ammonium allyloxypolyethoxy(10)sulphate, laurethoxy(23)methacrylate, laurethoxy(25)methacrylate, allyl methacrylate, and hydroxyl ethyl methacrylate, glycidyl methacrylate, ammonium salt of  $\alpha$ -sulfo- $\omega$ -[1-(Alkoxy)methyl-2-(2-propenyloxy)ethoxy]- $\omega$ -hydro-poly(oxy-1,2,-ethanediyl), ammonium salt of  $\alpha$ -[1-(Alkoxy)methyl-2-(2-propenyloxy)ethoxy]- $\omega$ -hydro-poly(oxy-1,2,-ethanediyl).

59. A method according to claim 55, wherein said at least one other monomer is selected from the group consisting of acrylic monomers and vinyl acetate.

60. A method according to the preceding claim, wherein said acrylic monomer is selected from the group consisting of acrylamide, acrylic acid, acrylonitrile, butyl acrylate, ethyl acrylate, 2-ethyl hexyl acrylate, and methyl methacrylate.

61. A method according to claim 55, wherein said at least one other monomer is of the formula  $R_1CH=CR_2C(O)A$ , wherein

A is selected from the group consisting of  $OR_3$ ,  $NR_3R_4$ , and  $CN$ ; and

$R_1$  and  $R_2$  are each independently selected from H and alkyl, said alkyl being linear or branched, and each of  $R_3$  and  $R_4$  independently may be H, alkyl, alkenyl, alkoxy, polyalkoxy, alkanol, or ether, each of which may be linear or branched, substituted or unsubstituted.

62. A method according to the preceding claim, wherein the carbon-containing R groups have between 1 and 15 carbons.

63. A method according to the preceding claim, wherein the alkyl groups have between 1 and 4 carbon atoms.

64. A method according to any one of claims 45 to 63, comprising:

- (i) dissolving said first monomer in a first liquid to obtain a solution, wherein said first liquid includes said second monomer optionally together with surfactants;
- (ii) mixing said solution with water and optionally also with surfactants to obtain a stable emulsion comprising water, surfactants, and said first monomer; and



- (iii) reacting said stable emulsion with an initiator to obtain an aqueous dispersion of a co-polymer containing at least said first monomer and said second monomer.

65. A method according to the preceding claim, wherein said first liquid does not include surfactants and in (ii) said solution is mixed with water and surfactants.